

EXHIBIT 4

United States Patent [19]**Fant**[11] **Patent Number:** **4,746,562**[45] **Date of Patent:** **May 24, 1988**[54] **PACKAGING FILM**[75] **Inventor:** Ennis M. Fant, Greenville, S.C.[73] **Assignee:** W. R. Grace & Co., Cryovac Div.,
Duncan, S.C.[21] **Appl. No.:** 834,694[22] **Filed:** Feb. 28, 1986[51] **Int. Cl.⁴** B32B 7/02[52] **U.S. Cl.** 428/213; 428/35;
428/339; 428/475.5; 428/476.9; 428/476.1;
428/516[58] **Field of Search** 428/516, 339, 476.1,
428/213, 475.5, 476.9, 35; 152/244.11[56] **References Cited****U.S. PATENT DOCUMENTS**

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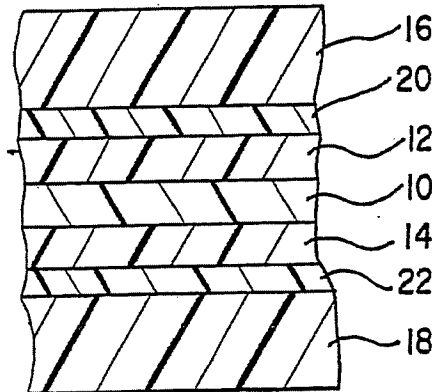
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Primary Examiner—Edith Buffalow*Attorney, Agent, or Firm*—John J. Toney; William D.
Lee, Jr.; Mark B. Quatt

[57]

ABSTRACT

A multilayer film useful in the packaging of high acid food products at elevated temperatures comprises a core layer of ethylene vinyl alcohol copolymer, two intermediate layers each comprising a polyamide; outer blend layers of linear low density polyethylene and anti-blocking agent, and adhesive polymeric materials to adhere the outer blend layers to the respective intermediate polyamide layers.

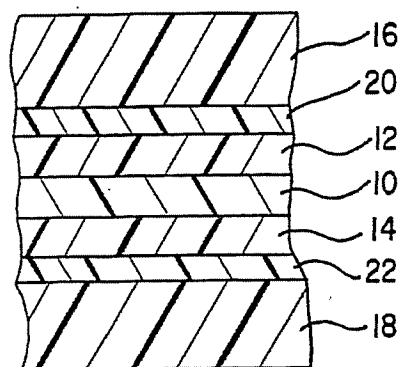
13 Claims, 1 Drawing Sheet

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FIG .1



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PACKAGING FILM

BACKGROUND OF THE INVENTION

This invention relates generally to the art of packaging films and more particularly to films useful in the packaging of food products.

It is common practice in packaging many goods, including food items, to use what is generally known as form-fill-seal equipment. In the vertical form-fill-seal arrangement, flexible packaging material is fed from a rollstock to a tube former where a tube is fashioned from the sheet material into a vertically dependent, upwardly open tube having overlapping longitudinal edges. These overlapping edges are subsequently sealed together longitudinally by means well known in the art and the end of the tube is sealed together by a pair of transverse heat seals which are vertically spaced apart. At this point the tube is filled with a measured quantity of the product to be packaged. A second heat sealing operation, typically performed after the filled tube has been downwardly advanced, completes enclosure of the product. Simultaneously with or shortly after the transverse heat sealing step the tube is completely transversely severed by known cutting means in a space between the vertically spaced apart pair of transverse heat seals. Thereafter the tube is downwardly advanced and the cycle is successively repeated so as to form a multiplicity of individually packaged products.

Alternatively, a single transverse heat seal including a pair of horizontally spaced apart sealing jaws may be used to form in effect two vertically adjacent heat seals which are simultaneously or subsequently severed at a line vertically intermediate the heat seals.

Flexible packaging material useful for this as well as other applications typically must meet stringent requirements imposed by the particular food or other article to be packaged. In some cases, for example in high acid foods such as tomato paste and other tomato products, the package must be capable of adequately protecting the food item after packaging and through the distribution cycle until the packaged product reaches the end user at point of sale.

Additionally, products such as those described above are sometimes introduced into the formed tube at relatively high temperatures of about 200° F. The formed package must be able to withstand the still relatively high temperatures of the food product immediately after packaging, and subsequent cooling operations to bring the package to room temperature or other desired temperature range.

The flexible material must also have sufficient abuse resistance to physical and mechanical abuse imposed by the entire form-fill-seal or other packaging system, and the subsequent abuse which the package may undergo during the distribution cycle.

Yet another requirement of packaging material, especially in form-fill-seal systems, is good heat sealability with respect to the transverse heat seals, which are typically subjected to loading forces from the introduced product such as food product, soon after the heat seal is formed.

Of interest in U.S. Pat. No. 4,284,674 issued to Sheptak and disclosing a multilayer film having a core layer of ethylene vinyl alcohol copolymer adhered on each side to nylon, each nylon layer in turn being adhered to a chemically modified polyolefin, and a further layer of primer material suitable to adhere the modified polyole-

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fin to an outer layer of polypropylene or other materials suitable for conveying toughness, flex-crack resistance and moisture barrier properties to the multi-ply film.

Also of interest in U.S. Pat. No. 4,355,721 issued to Knott et al and disclosing a coextruded multilayer sheet having a first layer of nylon, an EVOH barrier layer, another layer of nylon, and adhesive layer, and another outside layer of, for example, high density polyethylene.

Of interest is U.S. Pat. No. 4,398,635 issued to Hirt and disclosing a medication package in which a coextruded multiple layer sheet may have a structure including a layer of ethylene vinyl alcohol copolymer sandwiched between adjacent layers of nylon, and in which one of the nylon layers may be further adhered to a tie resin. The nylon layers may form either an outside surface or, in one example, internal layers with additional layers of polymeric materials added to each side of the sandwich structure.

Of interest is U.S. Pat. No. 4,407,873 issued to Christensen et al, disclosing a packaging material for retort applications including a heat seal layer of linear low density polyethylene, a second layer of linear low density polyethylene with optionally 0% to 80% medium density polyethylene blended into the second layer, a third layer of anhydride modified medium density polyethylene, a fourth layer of nylon, a fifth layer of ethylene vinyl alcohol copolymer, and a sixth layer of nylon.

Of interest is U.S. Pat. No. 4,457,960 issued to Newcome, disclosing a multilayer film having a core layer of a barrier material such as EVOH and EVOH blends. This film may be shrinkable and may be melt extruded, and may contain outside layers having a blend of linear low density polyethylene and ethylene vinyl acetate copolymer.

Of interest is U.S. Pat. No. 4,495,249 issued to Ohya et al, disclosing a five-layer film having a core layer of a saponified copolymer of ethylene and vinyl acetate, outer layers of a mixture of linear low density polyethylene and ethylene vinyl acetate copolymer, and two adhesive layers disposed between the core layer and outer layers.

It is an object of the present invention to provide a multilayer film suitable for the packaging of food products, especially high acid content food products at relatively high temperatures.

It is a further object of the present invention to provide a multilayer film useful in connection with form-fill-seal processes especially vertical form-fill-seal processes.

It is still another object of the present invention to provide a multilayer film which provides extended shelf life to food products such as high acid content food products.

It is yet another object of the present invention to provide a multilayer film which can be made into a package for food products which can be reheated in boiling water without delamination or breakage.

One particularly useful feature of this package is its usefulness in packaging food products currently packaged in metal packaging such as No. 10 metal cans. These cans tend to be expensive, bulky during shipment and, after use of the contained food product, difficult to dispose of. Utilizing the multilayer film of the present invention, many food products now packaged in the No. 10 can be conveniently and quickly packaged, stored, shipped, marketed, and sold to the end user such

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as a commercial or institutional user or a consumer. After use, the emptied package made from the multilayer film provides a much less bulky package for disposal.

SUMMARY OF THE INVENTION

In accordance with the present invention, a multilayer film comprises a core layer comprising an ethylene vinyl alcohol copolymer; two intermediate layers each comprising a polyamide; two surface layers each comprising a blend of a linear low density polyethylene and an anti-blocking agent; and each of said intermediate layers adhered to a respective surface layer by a layer of adhesive polymeric material.

In another aspect of the present invention, a method of making a seven-layer film comprises feeding an ethylene vinyl alcohol melt through a first extruder to a coextrusion die; feeding a polyamide melt through a second extruder to the coextrusion die; feeding a melt of an adhesive polymeric material through a third extruder to the coextrusion die; feeding a blend of linear low density polyethylene and an anti-blocking agent, as a melt, through fourth and fifth extruders to the coextrusion die; extruding the seven layer film from the coextrusion die; cooling the coextruded film; collapsing the cooled film; and gathering the collapsed film on a take-up means.

DEFINITIONS

The terms "linear low density polyethylene", "LLDPE", and the like are used herein to refer to copolymers of ethylene with one or more comonomers selected from C₄ to C₁₀ alphaolefins such as butene-1, octene, etc. in which the molecules of the copolymers comprise long chains with few side chain branches or cross-linked structures. This molecular structure is to be contrasted with conventional low or medium density polyethylenes which are more highly branched than their respective counterparts. "LLDPE" as defined herein has a density usually in the range of from about 0.916 grams per cubic centimeter to about 0.925 grams per cubic centimeter.

The term "polyamide" refers to high molecular weight polymers having amide linkages along the molecular chain, and refers more specifically to synthetic polyamide such as various nylons.

The terms "intermediate layer", "interior layer", and the like are used herein to define a layer in a multilayer film bounded on both sides by other layers.

The terms "anti-blocking agent" and the like are used herein to describe substances that reduce the tendency of films or sheets of polyolefin film to stick or adhere to each other or to other surfaces when such adhesion is otherwise undesirable. Typical chemicals such as colloidal silica, finely divided silica, clays, silicones, and certain amides and amines are useful in this application.

BRIEF DESCRIPTIONS OF THE DRAWINGS

Details of the present invention are provided by reference to the sole drawing figure where FIG. 1 represents a schematic cross-section of a preferred embodiment of a multilayer film of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The film structure depicted in FIG. 1 is directed to a multilayer film which is preferably palindromic or symmetrical in construction. A film structure is directed to

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a multilayer film having the generalized structure of A/B/C/D/C/B/A where A is an outer layer, B is an adhesive layer, C is an intermediate layer, and D is a barrier core layer. Preferably, the outer layers A each comprise about 26% of the total multilayer film thickness; the adhesive layers B each comprise about 8% of the total film thickness; the intermediate layers C each comprise about 11% of the total film thickness; and the barrier core layer D comprises about 10% of the total film thickness. The multilayer film of the present invention is preferably about 5 mils thick.

Preferably, core layer 10 is an ethylene vinyl alcohol copolymer having an ethylene content of preferably 32%. Commercially available resins suitable for the core layer include EVAL EC-F101 (EVALCA), Nippon Goshei Soarnol D, DT, and ZL, and Solvay Clarence R. Ethylene content for the EVOH is preferably between about 20% and 40%, and more preferably between about 25% and 35%. An ethylene content of about 32% by weight is most preferred.

Intermediate layers 12 and 14 are polyamides such as nylon 6. Various nylons are suitable in connection with the present invention including high viscosity versions and nylon copolymers. The polyamide of the intermediate layers 12 and 14 adds strength to the resulting multilayer film structure.

Outer layers 16 and 18 comprise a linear low density polyethylene blended with an anti-blocking agent. This blend contributes pliability to the resulting film, and has the quality of permitting heat sealing of the film even in the presence of contamination in the sealing area of the film. Several anti-blocking agents are available for use in connection with the outer blend layers 16 and 18. Particularly useful are micron-sized silica such as that available from Teknor Apex. This silica is available under the trade designation EPE-8160. Also commercially available is Syloid available from W. R. Grace & Co. A very suitable linear low density polyethylene is Dowlex 2035 available from Dow Chemical Company.

The anti-blocking agent of the outer layers (and of the third and fourth interior blend layers of nine layer embodiments), is necessary to prevent the multilayer film from sticking to the forming mandrel during a form-fill-seal operation, with the detrimental effect on filling operations which this would cause. A preferred range of the anti-blocking agent is from about 1% to about 15% by weight of the blend layers. A more preferred range is from about 5% to about 10%. Inadequate anti-blocking agent i.e. below 1%, will result in the film sticking to the forming mandrel or shoe as it is formed, and the film material will not machine well on form-fill-seal equipment. A content above 15% could result in a progressive decrease in seal strength.

Adhesive layers 20 and 22 may comprise various polymeric adhesives, especially modified polymeric adhesives such as Plexar 2581 available from Norchem. This particular adhesive is a LLDPE-based modified adhesive. LLDPE-based adhesives are preferred as adhesive materials in the present film. Adhesives based on other polyolefins can be used, but less effectively.

A method for making the film includes the step of blending the linear low density polyethylene resin and the anti-blocking agent in the proportions and ranges desired as discussed above. The resins are usually purchased from a supplier in pellet form and can be blended in any one of a number of commercially available blenders as is well known in the art. The anti-blocking agent

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is generally provided in particulate form for example as a powder.

The linear low density polyethylene resin and anti-blocking agent, as a blend, are then fed into the hoppers of two extruders which feed a coextrusion die. The ethylene vinyl alcohol copolymer resin, the polyamide resin, and the adhesive resin are likewise fed into respective extruders which feed the coextrusion die. For the preferred seven layer film having the two identical surface layers, two identical adhesive layers and two identical intermediate layers, and the core layer of ethylene vinyl alcohol copolymer, at least five extruders need to be employed. Additional extruders may be employed if a film having nonidentical adhesive or intermediate layers is desired. The materials are coextruded as a relatively thick tube or "tape" which has an initial diameter dependent upon the diameter of the coextrusion die. Circular coextrusion dies are well known to those in the art and can be purchased from a number of manufacturers. In addition to tubular coextrusion, slot dies could be used to coextrude the material in sheet form.

EXAMPLE 1

A sample film was prepared by blending 90% of LLDPE (Dowlex 2035), and 10% EPE-8160 anti-blocking agent. This outside blend layer was coextruded with a core layer containing EVAL F, and intermediate layers of Capron 8207 F, a nylon 6 resin available from Allied Corp. Plexar 3196 a linear low density polyethylene-based resin was used as an adhesive material.

The film exhibited an oxygen transmission rate averaging less than 0.2 cc STP/(24 hours, square meter, atmosphere) at 73° F., 0% RH (ASTM D 3985) at a total film gauge of about 5.15 mils. The film also had a water vapor transmission rate (grams/24 hours, 100 square inches at 100% RH) of about 0.36 at 100° F. (ASTM F 372) at a total film gauge averaging about 5.20 mils. Typical gauge of the barrier (EVOH) layer was 0.57 mils.

EXAMPLE 2

A second sample film was produced substantially as described in Example 1, but with Plexar 2581 in place of the Plexar used in the previous example.

EXAMPLE 3

A nine layer structure was produced substantially as described in Example 1, but having four blend layers of LLDPE and anti-blocking agent instead of only two such layers. The two outer layers of Example 3 were substantially the same as those in previous examples, but about half the thickness. On the interior or film side of each of the two outer layers, an additional layer of a blend of about 85% LLDPE and about 15% of another anti-blocking agent were provided, these third and fourth blend layers having about the same thickness as the two outer layers. The adhesive layers of this third sample film comprised Plexar 3196.

EXAMPLE 4

A fourth sample film was prepared substantially as described in Example 1, and comprising nine layers as in Example 3, but with the substitution of Dowlex 2037 for the Dowlex 2035 of the interior third and fourth blend layers of Example 3.

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The film of the present invention is preferably not stretch oriented, and therefore preferably a non-shrinkable film, especially in applications such as vertical form-fill-seal packaging. The film is also preferably unirradiated.

Various changes and modifications to the invention can be made by one skilled in the art without departing from the scope of the claims as presented below.

What is claimed is:

1. A multilayer coextruded film comprising:

(a) a core layer comprising an ethylene vinyl alcohol copolymer;

(b) two intermediate layers each comprising a polyamide;

(c) two outer layers each comprising a blend of from about 85% to about 99% of a linear low density polyethylene and from about 1% to about 15% of an anti-blocking agent; and

(d) two layers of adhesive polymeric material disposed between respective intermediate and outer layers.

2. The film of claim 1 wherein each of said outer layers comprises a blend of from about 90% to about 95% of said linear low density polyethylene, and from about 5% to about 10% of said anti-blocking agent.

3. The film of claim 1 wherein each of said outer layers comprises a blend of about 90% of said linear low density polyethylene, and about 10% of said anti-blocking agent.

4. The film of claim 1 wherein said core layer comprises an ethylene vinyl alcohol copolymer with an ethylene content of from about 20% to about 40%.

5. The film of claim 1 where said core layer comprises an ethylene vinyl alcohol copolymer with an ethylene content of from about 25% to about 35%.

6. The film of claim 1 wherein said core layer comprises an ethylene vinyl alcohol copolymer with an ethylene content of about 32%.

7. The film of claim 1 wherein said polyamide is nylon 6.

8. The film of claim 1 wherein said anti-blocking agent is silica.

9. The film of claim 1 wherein:

(a) the thickness of the core layer comprises about 10% of the total film thickness;

(b) the thickness of the two intermediate layers together comprises about 22% of the total film thickness;

(c) the thickness of the two outer layers together comprises about 52% of the total film thickness; and

(d) the thickness of the two adhesive layers together comprises about 16% of the total film thickness.

10. The film according to claim 9 wherein the total film thickness is about 5 mils.

11. A seven-layer coextruded film comprising:

(a) a core layer comprising an ethylene vinyl alcohol copolymer;

(b) two intermediate layers each comprising a polyamide;

(c) two outer layers each comprising a blend of from about 85% to about 99% of a linear low density polyethylene, and from about 1% to about 15% of an anti-blocking agent; and

(d) each of said intermediate layers adhered to a respective surface layer by an acid- or acid anhydride-modified polymeric adhesive.

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12. A seven-layer coextruded film suitable for use in packaging food products comprising:

- (a) a core layer comprising an ethylene vinyl alcohol copolymer;
- (b) two intermediate layers each comprising a polyamide;
- (c) two outer layers each comprising a blend of from about 90% to about 95% of a linear low density

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polyethylene, and from about 5% to about 10% of an anti-blocking agent; and

- (d) each of said intermediate layers adhered to a respective surface layer by an acid- or acid anhydride-modified polymeric adhesive.

13. The coextruded film according to claim 1 wherein a layer comprising a blend of linear low density polyethylene and an anti-blocking agent is disposed between each respective layer of adhesive polymeric material and an outer layer.

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EXHIBIT 5

United States Patent [19][11] **4,284,674****Sheptak**[45] **Aug. 18, 1981**[54] **THERMAL INSULATION**

[75] Inventor: Nicholas Sheptak, Appleton, Wis.

[73] Assignee: American Can Company, Greenwich, Conn.

[21] Appl. No.: 92,624

[22] Filed: Nov. 8, 1979

[51] Int. Cl.³ B32B 1/04; B32B 3/02; B32B 27/34; B32B 27/32

[52] U.S. Cl. 428/69; 52/309.5; 52/309.8; 52/309.9; 52/406; 220/467; 428/213; 428/268; 428/423.1; 428/423.5; 428/334; 428/336; 428/441; 428/442; 428/475.5; 428/476.1; 428/476.9; 428/516; 428/518; 428/520; 428/522; 428/523; 428/910

[58] Field of Search 428/69, 213, 216, 268, 428/325, 423.1, 423.5, 475.5, 476.1, 476.9, 516, 518, 520, 522, 523, 334, 336, 910, 911, 920, 421, 441, 442; 52/309.5, 309.8, 309.9, 406; 220/3, 467

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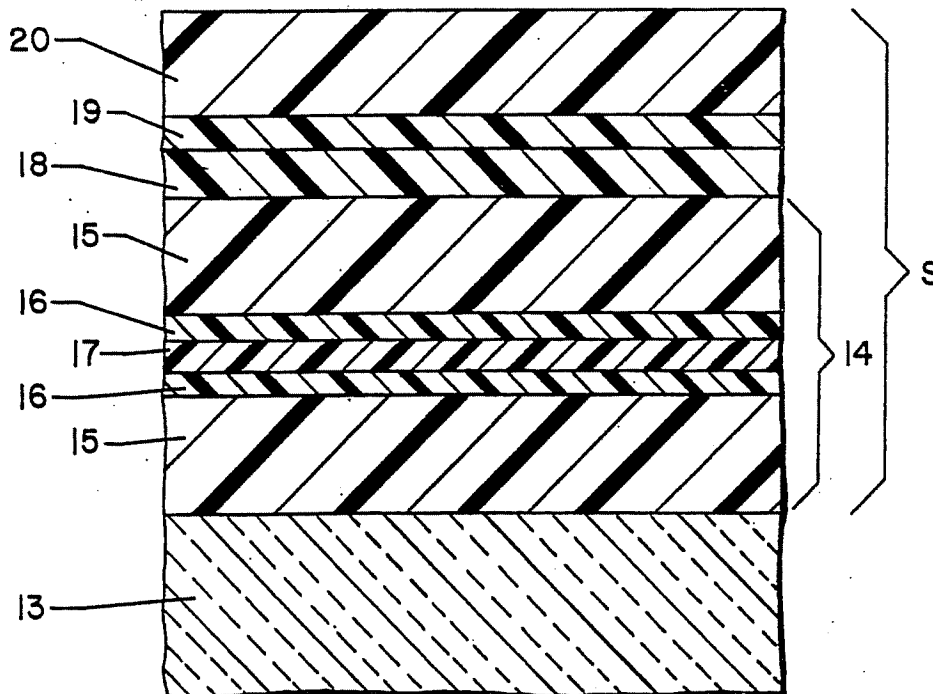
Re. 28,554	9/1975	Curler et al.	428/910 X
2,863,179	12/1958	Gaugler	52/406
2,939,811	6/1960	Dillon	428/69
3,004,877	10/1961	Simms et al.	428/69
3,075,857	1/1963	Fior et al.	428/476.3
3,264,165	8/1966	Stickel	428/69
3,514,367	5/1970	James	428/423.5
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4,058,647	11/1977	Inoue et al.	428/476.1

4,087,587	5/1978	Shida	428/500
4,087,588	5/1978	Shida	428/500
4,172,915	10/1979	Sheptak et al.	428/69

Primary Examiner—Ellis P. Robinson*Attorney, Agent, or Firm*—Robert P. Auber; Ernestine C. Bartlett; Ira S. Dorman[57] **ABSTRACT**

Hermetically sealed articles are provided which enclose a porous mass of material of relatively low heat conductivity and a charge of a gas having a coefficient of thermal conductivity lower than that of air and thoroughly permeating the porous mass of material or such sealed pouches may enclose only the porous mass of material evacuated down to about 10 mm. Hg. The pouches are useful as thermal insulation materials and are constructed of confronting sheets of multi-ply laminate material sealed along free edge portions thereof and comprising (1) a multi-layer film including a core layer of ethylene vinyl alcohol copolymer adhered on each side to nylon, each nylon layer being adhered to a layer of chemically modified polyolefin; (2) optionally, a low density polyethylene layer; (3) a layer of primer material suitable to effect adhesion between said modified polyolefin layer or polyethylene layer and the outer layer of oriented polypropylene or other material suitable for conveying toughness, flex crack resistance and moisture barrier properties to such multi-ply laminar construction.

The articles are useful as thermal insulation materials.

18 Claims, 3 Drawing Figures

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FIG. 1

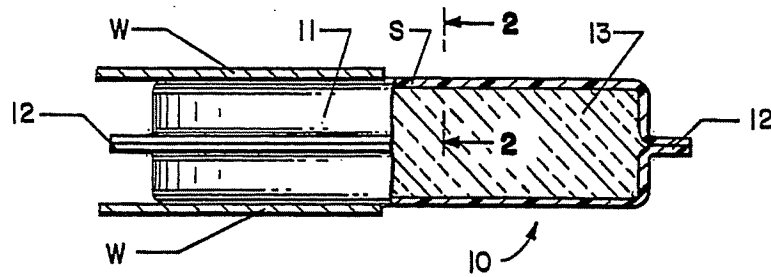


FIG. 2

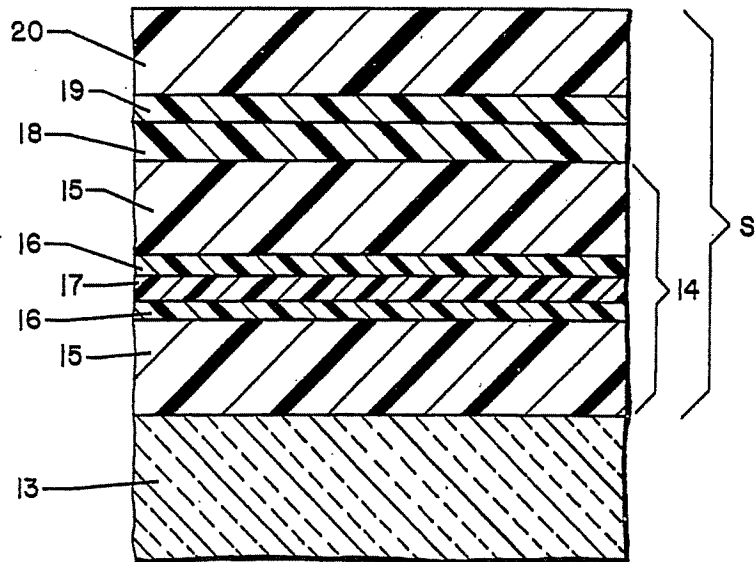
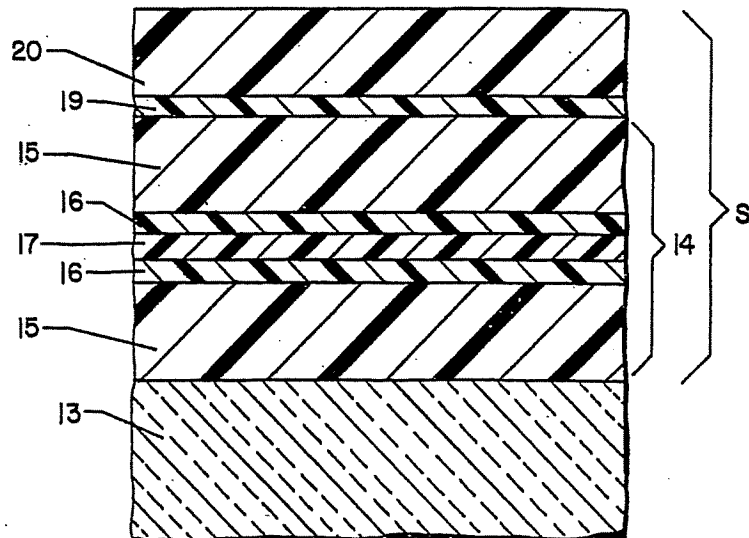


FIG. 3



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THERMAL INSULATION

BACKGROUND OF THE INVENTION

This invention relates to thermal insulation, and particularly to improvements in gas impervious pouch structure for containing a porous mass of thermal insulation or such a porous mass and a charge of gas having a coefficient of thermal conductivity lower than that of air.

Pouch structures containing insulation or insulation and gas as described have been found useful as insulation units for installation in the walls and doors of refrigerator cabinets. Such units both facilitate handling of the insulation and enhance performance of refrigerator cabinets and the like within which they are installed. These insulation units also have been found useful for other home appliances, such as, for example, freezers and water heaters, as well as for residential and commercial building structures.

Fibrous insulation comprising glass fibers or the like, in combination with an insulating gas such as difluorodichloromethane, commonly known as F-12 refrigerant, and enclosed in pouch structures of materials that are both gas and moisture impervious have been used.

The prior art is believed to be best exemplified by the following patents:

Dybvig	2,817,124	12/57
Sorel	2,966,439	12/60
Simms et al	3,004,877	10/61
Gaugler	2,863,179	12/58
Gaugler et al	2,779,066	01/57
Stickel	3,264,165	08/66
Bolsolas	4,054,711	10/77
Dillon	2,939,811	06/60
Jacobs	2,817,123	12/57
Strong et al	3,179,549	04/65
Janos	2,745,173	05/56

Dybvig, U.S. Pat. No. 2,817,124, discloses an insulating unit having two side by side compartments wherein the inner and outer walls of one compartment are comprised of Mylar coated on both sides with vapor deposited metal coating which in turn is coated with polyethylene, Saran or Hycar vinyl while the outer compartment is formed of polyethylene having pinholes of sufficient size to admit air.

Sorel, U.S. Pat. No. 2,966,439, discloses laminated products of normally thermoshrinkable polyvinylidene chloride film bonded in thermoshrunk condition to a normally dimensionally thermo-stable material such as fibrous sheet material.

Simms et al, U.S. Pat. No. 3,004,877, disclose heat insulating units for refrigeration cabinets comprising a porous mass and gas in a hermetically sealed bag formed of a multi-ply laminate including Kraft paper, Saran, Hycar vinyl cement and polyethylene.

Gaugler, U.S. Pat. Nos. 2,779,066 and 2,863,179, disclose heat insulating bags comprising double bags and double insulation and Freon gas comprising laminations of Mylar or vinyl chloride or vinyl acetate or Hycar vinyl; metal coating; Mylar or polystyrene; metal coating; Mylar or vinyl chloride or vinyl acetate or Hycar vinyl; Saran.

Stickel, U.S. Pat. No. 3,264,165, discloses insulating means comprising insulating material enclosed by Saran or a copolymer of vinyl chloride enclosed by Saran or a copolymer of vinyl chloride and vinyl acetate or

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Mylar adhered to a flexible closed-cell polyurethane film or multilayers of Kraft paper or foam; organic resin; metal coating; polyurethane foam; polyvinyl alcohol; metal coating; polyethylene.

Bolsolas, U.S. Pat. No. 4,054,711, discloses multilayer jacketing material for covering thermal insulation on pipes comprising a composite of metallized Mylar; adhesive; asbestos paper; glass scrim cloth; adhesive; polyvinyl fluoride film.

Jacobs, U.S. Pat. No. 2,817,123, discloses double bag constructions comprising an inner bag of laminated Mylar and Saran and an outer bag of fibrous insulation and polyethylene.

Dillon, U.S. Pat. No. 2,939,811, relates to heat-insulating units comprising hermetically sealed bags comprising deformable walls, a porous mass and gas wherein the bag comprises Saran, polyvinyl chloride, vinyl-nitrile rubber or polyethylene.

Strong et al, U.S. Pat. No. 3,179,549, disclose thermal insulating structures of the vacuum type comprising hermetically sealed containers having internal pressures of less than 100 microns mercury wherein the walls are low carbon steel and stainless steel.

Janos, U.S. Pat. No. 2,745,173, discloses vacuum insulation wherein the filler material is compressed before assembly and caused to retain its compressed form and wherein the walls of the structures are stainless steel or low carbon steel.

Prior art structures as represented by the above disclosures have been deficient in one or more aspects. Most of such constructions utilize Saran to meet moisture barrier problems and are thus accompanied by the problems generated by the shrinkability and tendency of Saran to become plastic at higher temperatures. Structures substituting or combining Mylar or other plastics have been subject to puncture by the fibrous insulating material. To overcome such problems, plastic film has been protected with metal coatings or polyurethane foam or relatively thick multi-ply laminations have been necessary or the multi-bag compartmented constructions have been proposed.

In U.S. Patent application Ser. No. 929,305 filed July 31, 1978 of Nicholas Sheptak and James E. Dewine, now U.S. Pat. No. 4,172,915 issued Oct. 30, 1979 improved unitary thermal insulating units are disclosed and claimed wherein the pouch is formed of a multi-ply laminate consisting essentially of an inwardly facing sealing layer of low density polyethylene; a layer of vinyl primer; a layer of metal foil; a layer of low density polyethylene; and an outwardly facing layer of Mylar or oriented polypropylene.

SUMMARY OF THE INVENTION

This invention is directed to an improvement over constructions as disclosed in said prior patents and said patent application Ser. No. 929,305, now U.S. Pat. No. 4,172,915. According to the invention, high barrier transparent structures are provided in which the barrier component is a multi-ply coextruded film barrier component comprising an ethylene vinyl alcohol core layer adhered on each side to a polyamide layer such as nylon which is in turn adhered to a layer of a chemically modified polyolefin.

A layer of low density polyethylene may, optionally, be adhered to the modified polyolefin layer or this polyethylene layer may be omitted. A layer of a material capable of conveying moisture barrier properties and

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capable of being adhered with a primer to the modified polyolefin layer or polyethylene layer, when present, is the outer layer of the construction. Preferably this outer layer will be oriented polypropylene.

Thermal insulating units are provided comprising a hermetically sealed pouch containing a porous mass of thermal insulation material and a charge of a gas having a coefficient of thermal conductivity lower than that of air enclosed in said pouch and permeating said porous mass of insulative material, the walls of said pouch being substantially impervious to said gas enclosed therein and to atmospheric gases and vapors. Alternatively, units are provided comprising a porous mass of thermal insulation material enclosed in a hermetically sealed pouch evacuated to a pressure of less than 100 microns of mercury prior to sealing.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a perspective showing, with parts broken away and sectioned, of an insulating unit embodying the invention;

FIG. 2 is an enlarged showing taken in the plane of line 2—2 in FIG. 1, as seen looking in the direction of arrows applied thereto and illustrating a multi-ply, laminated structure of a pouch of the invention; and

FIG. 3 is an enlarged showing similar to FIG. 2 and showing an alternative embodiment and modification of the pouch of FIG. 2.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

With reference to the drawing, there is seen in FIG. 1 spaced confronting walls W of a structure such as a refrigerator door panel, for example, between which there is disposed a pouch 10 made from a laminate sheet material embodying the invention, which pouch 10 includes a main portion 11 and a sealed peripheral portion 12. Pouch 10 conveniently is formed by sealing confronting surfaces of the free edge portions of a pair of rectangular sheets S of the material through application of heat and pressure in accordance with conventional practice. There is disposed within sealed pouch 10 a porous mass of material 13 of low-thermal conductivity, such as, for example, a fibrous mass of glass fibers. One such material is available under the trademark "FIBERGLAS", and preferably is formed as a batt of substantial thickness and resiliency. In one embodiment of the invention, a charge of a gas (not shown) having a coefficient of thermal conductivity lower than that of air is employed. The gas is preferably difluorodichloromethane, known in the trade as "F-12" and "R-12", which gas permeates the porous mass of glass fibers comprising batt 13.

In another embodiment of the invention, the permeating gas is omitted and the pouch 10 is evacuated down to 10 microns of mercury and hermetically sealed and employed without effect on insulating value.

With reference to FIGS. 2 and 3, the sheets S that define walls of the pouch are substantially impervious to the gas enclosed therein and to atmospheric gases and vapors and are unaffected by temperature changes over a wide range of variations. Such sheets provide high barrier, transparent structures that are fracture and/or puncture resistant and that retain such high barrier characteristics during and after processing into the finished package and upon subsequent handling. Such packages are designed for use as insulating panels in structures such as refrigerators which normally have a

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useful life in the nature of 10 to 20 years. It will therefore be apparent that the permeability characteristics of such sealed insulation articles must be such that are capable of being maintained over a substantial period of time without loss of permeating gas or without loss of vacuum and without admission of moisture, oxygen, etc.

The above characteristics are realized in the articles provided herein through the use of laminated sheet materials uniquely possessing toughness, flex crack resistance, sealability and high moisture and oxygen barrier properties.

The sheets S are comprised of multi-ply laminae consisting essentially of:

(1) a multi-layer coextruded cast film 14 varying in thickness from about 1.5 to 5.0 mils and preferably about 3 mils and comprising (a) a core layer 17 of ethylene vinyl alcohol copolymer film comprising from about 4% to 30% and preferably about 10% of the multi-layer film, adhered on each side to (b) a polyamide film layer 16, comprising from about 2 to 15% and preferably about 5% of the multi-layer film, each polyamide layer 16 being in turn adhered to (c) a layer 15 of chemically modified polyolefin film, comprising about 30% to 46% and preferably about 40% of the multi-layer film;

(2) optionally, a layer 18 of low density polyethylene film of about 0.5 to 2.0 mils and preferably about 1.0 mils adhered to the outer layer of the multi-layer film 14;

(3) a layer 19 of a suitable primer material of about 0.01 to 0.10 mils and preferably about 0.05 mils in thickness adhered to said polyethylene layer; and

(4) an outer layer 20 of a polymeric material possessing moisture barrier properties and capable of being adhered to said polyethylene layer with a suitable primer, said outer layer being about 0.4 to 1.25 mils and preferably about 1.25 mils in thickness.

In an alternative embodiment of the invention as illustrated in FIG. 3, the polyethylene layer 18 is omitted and the sheet is otherwise identical to that illustrated in FIG. 2.

The components of the sheets S each function to perform specific and critical functions in the pouches 10 formed therefrom. For example, the oriented polypropylene layer 20 which forms the outer surface of the pouch walls conveys toughness, flex crack resistance and moisture barrier properties to the sheets. The multi-layer film 14 comprising 5 layers of components, provides a core 17 of EVOH which provides gas barrier properties, a layer 15 of chemically modified polyolefin which provides heat sealability and a polyamide layer 16 which enhances adhesion between the core of EVOH, 17, and the chemically modified polyolefin layer, 16.

The multi-layer film 14 is quite thin and can be made by coextrusion as described in U.S. application Ser. No. 973,948 filed Dec. 28, 1978 and commonly assigned herewith. The film may be produced by melting resins of modified polyolefin, polyamide and ethylene vinyl alcohol and coextruding the same as a cast film. Heat sealing of the outer layers of modified polyolefin is readily obtained.

Ethylene vinyl alcohol polymers suitable for extrusion are commercially available. Kuraray of Japan produces an ethylene vinyl alcohol copolymer under the designation "EP-F" which has 32 to 36% ethylene, a molecular weight of 29,500 and melting point of 356° F.

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Other manufacturers produce suitable ethylene vinyl alcohol copolymers. One suitable copolymer has about 29% ethylene, a molecular weight of 22,000, and a melting point of 365° F. Another has about 40% ethylene, a molecular weight of 26,000, and a melting point of 327° F.

The polyamides which form the layers 16 may be any of commercially available materials well known as nylon. These polymers include polycapromamide, polyhexamethylene adipamide, poly-11-undecanoamide, poly-12-dodecanoamide, etc. and similar materials available commercially as nylon 6; nylon 6,6; nylon 6,10; nylon 6,15; etc.

The modified polyolefins which form the layers 15 adjacent the polyamide layers are blends of polyolefin and high density polyethylene (HDPE) grafted with an unsaturated fused ring carboxylic acid anhydride. The polyolefin component of the blend may include a number of resins such as high, low and medium density polyethylene and polyolefin copolymers such as ethylene vinyl acetate copolymer and ethylene acrylic acid. Modified polyolefin blends are disclosed in U.S. Pat. Nos. 4,087,587 and 4,087,588. Suitable modified polyolefins blends are available from the Chemplex Company of Rolling Meadows, Ill. under the name "PLEXAR". Commercially available grades of such modified polyolefins are blends of the graft with different polyolefins. These include Plexar-I, a blend with ethylene vinyl acetate copolymer; Plexar-II, a blend with high density polyethylene; Plexar-III further modified with an elastomer such as polyisobutylene; and Plexar-III, a blend with ethylene vinyl acetate polymer adapted for cast film coextrusion. Plexar III is the preferred component for the multi-layer film member 16 which is preferably formed by cast film coextrusion although it may also be formed by blown tube coextrusion or the like.

Sheets S herein are formed by priming the outer layer, for example, oriented polypropylene sheet 20 with a suitable primer material 19 and extrusion laminating the primed sheet material to either side of the multi-layer film 14 or by interposing low density polyethylene between the primed outer layer sheet material and the chemically modified polyolefin layer 15.

The sheet material comprising the outer layer of the construction may be any plastic material that is capable of conveying toughness and moisture barrier properties to the multi-layer construction S. Examples of such materials include oriented polypropylene, Saran (vinyl chloride-vinylidene chloride copolymer) coated oriented polypropylene, Saran coated oriented nylon, high density polyethylene and monochlorotrifluoroethylene, available commercially as "ACLAR" from Allied Chemical Co., of which oriented polypropylene is preferred.

Suitable primers include polyester/polyurethanes available commercially as Adcote 503C from Morton Chemical Co.; polyethylene imine available commercially as CHEMICAT P-145 from ALCOLAC; polyester/polyurethanes available commercially as "UNOFLEX" from Polymer Industries, Inc.; and the like.

Pouches 10 are formed from sheets S by any means conventional and well known in the art.

The barrier properties realized in the above described articles have been found to be held intact during processing of the laminate into the finished package and tests with freon filled packages as well as with high

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vacuum packages have demonstrated the utility of such structures for use as insulation packages.

While glass fiber insulation is preferred as the porous mass of thermally insulative material, it will be understood that mineral fiber as well as foamed type insulations are contemplated by the invention.

While various embodiments of the invention have been described, it will be understood that other modifications may be made without departing from the scope of the appended claims.

I claim:

1. A multi-ply laminate comprising:

(1) a multi-layer coextruded film consisting essentially of (a) a core layer of ethylene vinyl alcohol adhered on each side to (b) a polyamide layer, each such polyamide layer being adhered to (c) a layer of a modified polyolefin which consists of a polyolefin polymer or copolymer blended with polyethylene grafted with an unsaturated fused ring carboxylic acid anhydride;

(2) a layer of primer material effective to enhance adhesion between said modified polyolefin layer; and

(3) an adjacent outer layer of a plastic material capable of conveying toughness and moisture barrier properties to said laminate.

2. A multi-ply laminate of claim 1 wherein said plastic material forming said outer layer is oriented polypropylene, oriented polypropylene coated with vinyl chloride-vinylidene chloride copolymers, oriented nylon coated with vinyl chloride-vinylidene chloride copolymer, high density polyethylene and monochlorotrifluoroethylene.

3. A multi-ply laminate of claim 1 wherein said plastic material forming the outer layer is oriented polypropylene.

4. A multi-ply laminate of claim 1 additionally comprising a layer of low density polyethylene between said primer and modified polyolefin layer.

5. A multi-ply laminate of claim 1 wherein said modified polyolefin layer consists of ethylene vinyl acetate blended with polyethylene grafted with said acid anhydride.

6. A multi-ply laminate of claim 4 wherein said polyamide layer is nylon.

7. A multi-ply laminate comprising:

(1) a five-layer coextruded cast film of about 1.5 to 5 mils in thickness consisting essentially of a core layer of ethylene-vinyl alcohol comprising about 10% of the film thickness adhered on each side to nylon comprising about 5% of the film thickness, each nylon layer being adhered to a layer of modified polyolefin comprising ethylene vinyl acetate blended with high density polyethylene grafted with an unsaturated fused ring carboxylic acid anhydride, each of said modified polyolefin layers comprising about 40% of the film thickness;

(2) a layer of about 0.5 to 2.0 mils of low density polyethylene adhered to one side of one of said modified polyolefin layers;

(3) a layer of about 0.01 to 0.10 mils of a polyester-polyurethane primer adhered to said polyethylene layer; and

(4) an outwardly facing layer of oriented polypropylene adhered to said primer layer.

8. A multi-ply laminate comprising:

(1) a five-layer coextruded cast film of about 1.5 to 5.0 mils in thickness consisting essentially of a core

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layer of ethylene-vinyl alcohol comprising about 10% of the film thickness adhered on each side to nylon comprising about 5% of the film thickness, each nylon layer being adhered to a layer of modified polyolefin comprising ethylene vinyl acetate blended high density polyethylene grafted with an unsaturated fused ring carboxylic acid anhydride, each of said modified polyolefin layers comprising about 40% of the film thickness;

(2) a layer of about 0.01 to 0.10 mils of a polyester-polyurethane primer adhered to said modified polyolefin layer; and

(3) an outwardly facing layer of oriented polypropylene adhered to said primer layer.

9. In a thermal insulating unit comprising a porous mass of thermally insulative material and a sealed pouch hermetically enclosing said porous mass; the improvement which comprises providing a heat sealed, puncture resistant insulating unit having vapor and gas barrier properties wherein the pouch is formed of a multiply laminate of claim 1.

10. The improvement as claimed in claim 9 wherein said insulating unit also seals a charge of gas having a coefficient of thermal conductivity lower than that of air which permeates the porous mass of insulative material.

11. The improvement as claimed in claim 10, wherein said permeating gas is difluorodichloromethane.

12. The improvement as claimed in claim 9 wherein said pouch containing said insulative material is evacu-

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ated to a pressure less than 100 microns of mercury prior to formation of the hermetic seal.

13. In a thermal insulative unit comprising a porous mass of thermally insulative material; a charge of gas having a coefficient of thermal conductivity lower than that of air and permeating said porous mass of insulative material, and a sealed pouch hermetically enclosing said porous mass; the improvement which comprises providing said insulative material and said gas in a heat sealed, puncture resistant, vapor and gas barrier insulating unit wherein the pouch is formed of a multi-ply laminate as claimed in claim 7.

14. The improvement as claimed in claim 13 wherein the insulative material comprises glass fiber.

15. The improvement as claimed in claim 13 wherein the gas is difluorodichloromethane.

16. In a thermal insulative unit comprising a porous mass of thermally insulative material and a sealed pouch hermetically enclosing said porous mass of insulative material; the improvement which comprises providing said insulative material in a heat sealed, puncture resistant, vapor and gas barrier insulating unit wherein the pouch is formed of a multi-ply laminate as claimed in claim 8.

17. The improvement as claimed in claim 16 wherein the insulative material comprises glass fibers.

18. The improvement as claimed in claim 16 wherein said pouch containing said insulative material is evacuated to a pressure of less than 100 microns of mercury prior to formation of the hermetic seal.

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EXHIBIT 6

EXHIBIT 6

REDACTED IN ITS ENTIRETY

EXHIBIT 7

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IN THE UNITED STATES DISTRICT COURT

FOR THE DISTRICT OF DELAWARE

CRYOVAC, INC.,

Plaintiff/Counter-Defendant,

-vs-

Civil Action

No. 04-1728-KAJ

PECHINEY PLASTIC PACKAGING, INC.,

Defendant/Counter-Plaintiff.

NOTE: PORTIONS OF TEXT DEEMED CONFIDENTIAL -

SUBJECT TO PROTECTIVE ORDER

The videotaped deposition of ELDRIDGE MOUNT, III,
called by the Plaintiff/Counter-Defendant for examination,
pursuant to notice and pursuant to the Federal Rules of
Civil Procedure for the United States District Courts pertaining
to the taking of depositions, taken before Cynthia J. Conforti,
Certified Shorthand Reporter, at One IBM Plaza, Chicago, Illinois,
commencing at the hour of 9:02 a.m. on the 4th day of August, A.D., 2005.

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<p style="text-align: right;">38</p> <p>1 THE WITNESS: I guess I'm not sure until I</p> <p>2 read it.</p> <p>3 BY MR. FUCHS:</p> <p>4 Q. Okay. Would you turn to Fant's</p> <p>5 deposition — excuse me. 09:38AM</p> <p>6 Would you turn to the Fant transcript,</p> <p>7 Mount Deposition Exhibit 4, at page 132.</p> <p>8 A. Okay.</p> <p>9 Q. You see lines — page 132, line 14</p> <p>10 Mr. Fant was asked: 09:39AM</p> <p>11 Could you place before you Fant Exhibit</p> <p>12 Number 3. That was your United States Patent</p> <p>13 Number 4,746,562? Do you have that in front of</p> <p>14 you.</p> <p>15 Answer: Yes, sir.</p> <p>16 A. Yes, sir, um-hmm.</p> <p>17 Q. And then do you see Mr. Fant was then</p> <p>18 asked:</p> <p>19 Was the film described in your patent 09:39AM</p> <p>20 oriented or not oriented?</p> <p>21 A. Yes.</p> <p>22 Q. And do you see Mr. Fant's answer was that</p>	<p style="text-align: right;">40</p> <p>1 and sheets.</p> <p>2 BY MR. FUCHS:</p> <p>3 Q. Was the material made in the Fant patent</p> <p>4 oriented by heating the material and stretching it 09:41AM</p> <p>5 to realign the molecular configuration by a</p> <p>6 racking or blown bubble process?</p> <p>7 MR. TRYBUS: Object to the form of the</p> <p>8 question.</p> <p>9 THE WITNESS: I believe that the polymers 09:41AM</p> <p>10 were heated, melted and coextruded and then drawn</p> <p>11 from the face of the die so that there was some</p> <p>12 molecular orientation induced in the region</p> <p>13 between the die lip and the place where the</p> <p>14 polymer was solidified. 09:42AM</p> <p>15 They speak of an initial diameter, and</p> <p>16 they don't — so I believed it was heated and</p> <p>17 melted and then coextruded, and the orientation</p> <p>18 occurred between the exit of the die and the point</p> <p>19 at which it was frozen.</p> <p>20 BY MR. FUCHS:</p> <p>21 Q. So you — in reading the Fant patent you</p> <p>22 thought they pulled the film out of the</p>
<p style="text-align: right;">39</p> <p>1 the film was not oriented?</p> <p>2 A. That's what he says. 09:39AM</p> <p>3 Q. Who would be in a better position to know</p> <p>4 whether the film made by the Fant patent was</p> <p>5 oriented or not oriented, you or Mr. Fant?</p> <p>6 MR. TRYBUS: Object to the form of the</p> <p>7 question. 09:40AM</p> <p>8 THE WITNESS: I think someone who had</p> <p>9 measured the molecular orientation.</p> <p>10 BY MR. FUCHS:</p> <p>11 Q. Did you do that?</p> <p>12 A. No, I didn't. 09:40AM</p> <p>13 Q. Do you actually have an opinion that the</p> <p>14 Fant patent produced by the method described in</p> <p>15 the Fant patent is an oriented or not oriented</p> <p>16 film?</p> <p>17 MR. TRYBUS: Object to the form of the</p> <p>18 question.</p> <p>19 THE WITNESS: It's my opinion that it most</p> <p>20 likely contains some molecular orientation due to</p> <p>21 the manufacturing technique that was used and the 09:40AM</p> <p>22 difficulty of making nonmolecularly oriented tubes</p>	<p style="text-align: right;">41</p> <p>1 coextruder; is that correct? 09:42AM</p> <p>2 A. Yes, I think it would be — I know it's</p> <p>3 very difficult to — you have to remove the melt</p> <p>4 from the die face. It's very difficult, extremely</p> <p>5 difficult to pull it without changing the</p> <p>6 dimensions of the tube, the thickness or the 09:42AM</p> <p>7 diameter. Even if it was under gravity, there</p> <p>8 would be some thinning.</p> <p>9 Q. Have you had any personal experience with</p> <p>10 pulling such a film from such a coextruder as</p> <p>11 described in Fant? 09:42AM</p> <p>12 A. Generally more often with a flat die, but</p> <p>13 occasionally with a circular die.</p> <p>14 Q. What does Fant use?</p> <p>15 A. He uses a circular die.</p> <p>16 Q. And do you have any personal experience in 09:43AM</p> <p>17 what happens when you pull the film from such a</p> <p>18 circular die?</p> <p>19 A. Yes.</p> <p>20 Q. Would you turn to page 36 of the</p> <p>21 Exhibit 4, the Fant transcript?</p> <p>22 A. Okay.</p>

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<p style="text-align: right;">74</p> <p>1 descriptions.</p> <p>2 Q. In Column 5, at line 16, when they</p> <p>3 coextrude two different polymeric material, they</p> <p>4 say "coextruded film laminate," correct?</p> <p>5 A. Yes. 10:33AM</p> <p>6 Q. And in Column 3, line 48, when they refer</p> <p>7 to laminates, they don't say "coextruded</p> <p>8 laminates," do they?</p> <p>9 A. They allow all sorts of laminates.</p> <p>10 Q. But they don't specifically use the 10:33AM</p> <p>11 terminology "coextruded laminate," correct?</p> <p>12 A. They don't say coextrusion there, no.</p> <p>13 Q. Okay.</p> <p>14 I'd like to now turn to another patent,</p> <p>15 the Yazaki '610 patent which I'll mark as Mount</p> <p>16 Exhibit Number 6.</p> <p>17 (Whereupon Exhibit 6 was</p> <p>18 marked for identification.)</p> <p>19 BY MR. FUCHS: 10:36AM</p> <p>20 Q. Now, the Yazaki '610 patent does teach a</p> <p>21 seven-layer structure; isn't that correct?</p> <p>22 A. Let's see, if I look at my report, yes, on</p>	<p style="text-align: right;">76</p> <p>1 specifically discloses two structures which would</p> <p>2 have been understood by one of ordinary skill in</p> <p>3 the art to be symmetrical in the layer</p> <p>4 arrangement. Do you see that? 10:38AM</p> <p>5 A. Yes.</p> <p>6 Q. Okay.</p> <p>7 A. Whose -- are there -- I know that there</p> <p>8 are several...</p> <p>9 Q. Well, it was your opinion that this 10:38AM</p> <p>10 structure depicted in Column 7 of the Yazaki '610</p> <p>11 patent was symmetrical in the layer arrangement,</p> <p>12 correct?</p> <p>13 A. Under my description of symmetrical, yes.</p> <p>14 Q. I think it would have been everybody's, 10:38AM</p> <p>15 but that's beside the point. Yours is the only</p> <p>16 one who's giving any testimony today.</p> <p>17 A. I believe that is the point.</p> <p>18 Q. Okay. Well --</p> <p>19 A. The example, if you look a little bit</p> <p>20 lower down in Column 7, they give the ratios of</p> <p>21 the thickness of the different layers, so --</p> <p>22 Q. Well, let's look at that.</p>
<p style="text-align: right;">75</p> <p>1 26, page 26, yes, a seven-layer film structure,</p> <p>2 um-hmm. 10:36AM</p> <p>3 Q. Okay. And that's at Column 7, lines 23 to</p> <p>4 25, correct?</p> <p>5 A. That's what I have, yes.</p> <p>6 Q. And then you also opine in your expert</p> <p>7 report that this seven-layer structure referred to 10:37AM</p> <p>8 at Column 7 of the Yazaki patent is arranged</p> <p>9 symmetrically; is that correct?</p> <p>10 A. Under whose -- under whose description of</p> <p>11 "arranged symmetrically"?</p> <p>12 Q. I was looking at your report at page 26. 10:37AM</p> <p>13 A. So under mine?</p> <p>14 Q. Just refer to your report at page 26. Do</p> <p>15 you have it -- you see it? It's right there.</p> <p>16 A. Yes.</p> <p>17 Q. Do you see where you say:</p> <p>18 The 4,511,610 patent recites in Column 7,</p> <p>19 lines 23, dash, 25 seven-layer structures of, and</p> <p>20 then you give the structure. Do you see that?</p> <p>21 A. Yes. 10:38AM</p> <p>22 Q. And you say: Therefore, the '610 patent</p>	<p style="text-align: right;">77</p> <p>1 Do you see it says: The thickness of each 10:39AM</p> <p>2 layer is not particularly critical in the</p> <p>3 multilayer vessel. Do you see that?</p> <p>4 A. Yes.</p> <p>5 Q. Okay. And even though the thickness of</p> <p>6 the layer was not particularly critical, you were 10:39AM</p> <p>7 still able to arrive at the opinion that the</p> <p>8 structure was symmetrical in the layer</p> <p>9 arrangement, correct?</p> <p>10 MR. TRYBUS: Object to the form of the</p> <p>11 question. 10:39AM</p> <p>12 THE WITNESS: In the layer ratios that</p> <p>13 they present, they present uniform -- the A to B</p> <p>14 thickness ratio in a given range and the B to C in</p> <p>15 a given range.</p> <p>16 BY MR. FUCHS: 10:39AM</p> <p>17 Q. You're referring to the next sentence</p> <p>18 which says:</p> <p>19 However, it is ordinarily preferred that</p> <p>20 the B-A thickness ratio be in the range of from 1</p> <p>21 to 1 to 500 to 1 and the B-C thickness ratio be in</p> <p>22 the range of from 1 to 1 to 500 to 1, you're</p>

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<p style="text-align: right;">242</p> <p>1 Q. But there is a difference --</p> <p>2 A. There seems to be a difference in the 03:42PM</p> <p>3 words, yes, and I -- yes.</p> <p>4 Q. Could you turn to page 20 of your report.</p> <p>5 A. Okay.</p> <p>6 Q. You see the heading Design and Function of</p> <p>7 Asymmetric Outer Layers. Do you see that? 03:43PM</p> <p>8 A. I do.</p> <p>9 Q. See the second sentence where you write:</p> <p>10 There is a real need and requirement that</p> <p>11 the inner layer of a packaging film have different</p> <p>12 properties than the outer surface of the packaging 03:43PM</p> <p>13 film. Do you see that?</p> <p>14 A. I do.</p> <p>15 Q. Would one of ordinary skill in the art in</p> <p>16 1986 have known that?</p> <p>17 A. Absolutely, especially the person of --</p> <p>18 the imaginary person, the person of ordinary skill</p> <p>19 in the art used to define and know the meanings,</p> <p>20 but that was a very well-known feature of the</p> <p>21 design of packaging films. 03:43PM</p> <p>22 Q. And that was obvious that you could need</p>	<p style="text-align: right;">244</p> <p>1 Q. I believe it's the last sentence on the 03:44PM</p> <p>2 page.</p> <p>3 A. Therefore, the concept of asymmetric</p> <p>4 surface properties has been well known to one of</p> <p>5 ordinary skill in the art?</p> <p>6 Q. We're in different places. 03:44PM</p> <p>7 A. Sorry.</p> <p>8 Q. Okay. I was focusing on the last sentence</p> <p>9 of the page.</p> <p>10 A. Okay.</p> <p>11 Q. And you see there you write: 03:44PM</p> <p>12 In general, packaging films will have slip</p> <p>13 and antiblock modification on both the inner and</p> <p>14 outer film surfaces. Do you see that?</p> <p>15 A. Yes, I do.</p> <p>16 Q. And that was also well-known in 1986, 03:45PM</p> <p>17 correct?</p> <p>18 A. Yes, and it would have been well-known to</p> <p>19 the person of ordinary skill in the art.</p> <p>20 Q. And you see later in that sentence you</p> <p>21 say:</p> <p>22 The levels of slip and antiblock would be</p>
<p style="text-align: right;">243</p> <p>1 different properties in the two outer layers in</p> <p>2 the mid 1980s, correct?</p> <p>3 A. Unless you --</p> <p>4 MR. TRYBUS: Object to the form of the 03:43PM</p> <p>5 question.</p> <p>6 THE WITNESS: Excuse me.</p> <p>7 Unless you would put a piece of film on a</p> <p>8 packaging machine, and if it wasn't -- if the</p> <p>9 properties weren't right, the differences between 03:43PM</p> <p>10 the inside and the outside, the film wouldn't run</p> <p>11 on a packaging machine.</p> <p>12 I had a case where inner and outer</p> <p>13 properties were very, very important and had to be</p> <p>14 modified. 03:44PM</p> <p>15 BY MR. FUCHS:</p> <p>16 Q. And if you look at -- in your last</p> <p>17 sentence on the page, it says:</p> <p>18 In general, packaging films will have slip</p> <p>19 and antiblock modification on both the inner and</p> <p>20 outer film surfaces. Do you see that?</p> <p>21 A. That's the -- is that the next-to-last</p> <p>22 sentence?</p>	<p style="text-align: right;">245</p> <p>1 different. Will be different.</p> <p>2 A. To get to differential properties.</p> <p>3 Q. And that was also known to persons of 03:45PM</p> <p>4 ordinary skill in the art in 1986, correct?</p> <p>5 A. Yes. My person of ordinary skill in the</p> <p>6 art or Dr. Kimmel's or your?</p> <p>7 Q. Since we don't have Dr. Kimmel here --</p> <p>8 A. We'll use mine. 03:45PM</p> <p>9 Q. -- we'll have to use yours?</p> <p>10 A. Okay. Well, my person of ordinary skill</p> <p>11 in the art certainly would have known and</p> <p>12 understood that.</p> <p>13 Q. Okay. And do you have the '419 patent 03:45PM</p> <p>14 still in front of you?</p> <p>15 A. Well, it's here.</p> <p>16 Q. Take a look. First one I gave you --</p> <p>17 A. Yeah, I have it.</p> <p>18 Q. Could you turn to Column 9. 03:46PM</p> <p>19 And do you see there in the '419 patent,</p> <p>20 it says: Obvious modifications to the invention</p> <p>21 as described may be made by one skilled in the art</p> <p>22 without departing from the spirit and the scope of</p>

EXHIBIT 8

United States Patent [19][11] **Patent Number:** **4,561,920****Foster**[45] **Date of Patent:** **Dec. 31, 1985**[54] **BIAXIALLY ORIENTED OXYGEN AND
MOISTURE BARRIER FILM**[75] **Inventor:** Ronald H. Foster, Minooka, Ill.[73] **Assignee:** Norchem, Inc. formerly Northern
Petrochemical Company, Omaha,
Nebr.[21] **Appl. No.:** 578,073[22] **Filed:** Feb. 8, 1984[51] **Int. Cl.⁴** B32B 31/00[52] **U.S. Cl.** 156/244.11; 156/244.24;
428/35; 428/516; 428/518; 428/349[58] **Field of Search** 428/35, 516, 349;
156/244.11, 244.24[56] **References Cited****U.S. PATENT DOCUMENTS**

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[57]

ABSTRACT

A biaxially oriented oxygen and moisture barrier film and a method of producing such a film which comprises co-extruding at least one polyolefin polyolefin layer, at least one layer of an ethylene vinyl alcohol copolymer with a melt flow rate of at least about 8 grams per 10 minutes, and an adhesive layer wherein the layers are combined into a composite sheet with the adhesive interposed between the polyolefin layer and ethylene vinyl alcohol copolymer layers. Next, the composite sheet is immediately cooled so that the crystallinity of the ethylene vinyl alcohol copolymer is no more than about 25 percent. Finally, the composite sheet is biaxially oriented in the longitudinal direction to a degree of about 2:1 to about 4:1 and in the transverse direction to a degree of about 3:1 to about 7:1.

14 Claims, No Drawings

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BIAXIALLY ORIENTED OXYGEN AND MOISTURE BARRIER FILM

BACKGROUND OF THE INVENTION

The present invention relates to a method for producing a biaxially oriented oxygen and moisture barrier film which is comprised of a polyolefin layer and an ethylene vinyl alcohol copolymer barrier layer. More particularly, the invention relates to a simple continuous method whereby the two layers are combined by co-extrusion and biaxially oriented at the same time.

Ethylene vinyl alcohol copolymer resins offer excellent barrier properties with respect to such gases as oxygen, carbon dioxide and nitrogen. In addition, they are also effective barriers against odors and the loss of flavor. Such resins, hereinafter referred to as EVOH resins, are moisture sensitive and the barrier properties are reduced in the presence of high humidity. Polypropylene offers excellent barrier properties with respect to moisture together with good strength properties and a high use temperature. When EVOH resins are encapsulated by layers of polypropylene, they are protected from moisture and therefore retain their barrier characteristics.

The biaxial orientation of EVOH resins enhances their barrier properties as well as reduces their susceptibility to moisture. The biaxial orientation of polypropylene increases its stiffness and enhances both its optical and other physical properties such as tensile strength, tear strength, and other mechanical properties.

In the past, others have attempted to produce biaxially oriented composite structures containing both polypropylene and EVOH resins by first producing a polypropylene sheet and orienting the sheet in the longitudinal direction. Then a layer of EVOH resin was either laminated or extrusion coated onto the polypropylene and the composite was then oriented in the transverse direction. This method of production is costly and only results in the orientation of the EVOH resin in one direction, thus not achieving the full benefit of biaxial orientation.

U.S. Pat. No. 4,239,826, issued Dec. 16, 1980, discloses a multi-layer barrier film comprising a barrier layer of substantially pure ethylene vinyl alcohol copolymer adhered between adjacent adherent layers consisting essentially of a partially hydrolyzed vinyl acetate polymer or copolymer. A layer of another material such as polypropylene can overlie the partially hydrolyzed vinyl acetate layers. The patent discloses co-extrusion of the EVOH and the partially hydrolyzed vinyl acetate polymer to form the multi-layer structure and then subsequent co-extrusion of the overlying material onto this structure. The patent does not suggest that this construction could be biaxially oriented and is otherwise distinguishable from the present invention because the adhesive is different, it does not mention controlling crystallinity of the EVOH, the percent ethylene of the products mentioned is too low for flexibility for biaxially oriented film, and, even if this film was to be biaxially oriented, the operation would be a two-step operation whereas the operation of the present invention is a one-step operation.

SUMMARY OF THE INVENTION

The present invention relates to a method of producing a biaxially oriented oxygen and moisture barrier film which comprises first co-extruding at least one polyole-

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fin layer of a polyolefin selected from the group consisting of polyethylene, polypropylene and copolymers of ethylene with other olefin monomers, at least one layer of an ethylene vinyl alcohol copolymer with a melt flow rate of at least about 8 grams per 10 minutes, and at least one adhesive layer wherein these layers are combined into a composite sheet with the adhesive interposed between the core layer and the EVOH. Next, the composite sheet is immediately cooled so that the crystallinity of the EVOH is no more than about 25%. Finally, the composite sheet is biaxially oriented in the longitudinal direction to a degree of about 2:1 to about 4:1 and in the transverse direction to a degree of about 3:1 to about 7:1. In a preferred embodiment of the invention, the ratio of the thickness of the adhesive to the thickness of the core layer is about 1:8 to about 1:15. The invention also relates to a biaxially oriented oxygen and moisture barrier film formed by the above method.

DETAILED DESCRIPTION OF THE INVENTION

The ethylene vinyl alcohol (EVOH) copolymers used in the present invention are the saponified or hydrolyzed product of an ethylene-vinyl acetate copolymer having, generally, an ethylene content of 25 to 75 mole percent. It is highly preferred that the percent ethylene in the EVOH be at least 45 percent so that the EVOH is flexible enough to be stretched during the orientation process. The degree of hydrolysis should reach at least 96 percent, preferably at least 99 percent. It is highly preferred that the degree of hydrolysis be greater than 96 percent because below that the barrier properties are less than optimum. It is extremely important to the performance of the present invention that the melt flow rate of the EVOH be at least 8 grams per 10 minutes at 190° C. and a load of 2,160 grams. If the melt flow rate is less than 8 grams per 10 minutes then the viscosities of the EVOH, adhesive, and core layer cannot be matched. It is important to match the viscosities of these materials to avoid interfacial instability which causes waviness of the melt and uneven distribution of the layers, otherwise known as melt fracture. The viscosity of these materials is most easily and effectively matched by monitoring the melt flow rate of the materials. At EVOH melt flow rates below 8 grams per 10 minutes, melt fracture occurs. It does not occur if the melt flow rate is higher.

The polyolefin layer used in the present invention can be of a polyolefin selected from the group consisting of polyethylene, including low density polyethylene, high density polyethylene, and linear low density polyethylene, polypropylene, and copolymers of ethylene with other olefins. The preferred polymers for use as the polyolefin layer are polypropylene and ethylene propylene copolymers containing predominately propylene. The melt flow rate of the polyolefin layer must not be so low that it is too stiff and thus unorientable. For propylene ethylene copolymers, it is preferred that the melt flow rate be from about 2.5 to about 6.0 grams per 10 minutes at 230° C. and a load of 2,160 grams. For polypropylene, it is preferred that the melt flow rate be from about 2.5 to about 4.5. In this range, the viscosities of the copolymer and the polypropylene are most compatible with EVOH and the adhesive. Also, in this range, orientation of the copolymer or the polypropylene results in the best properties.

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The adhesive used in the present invention should be selected from the group consisting of maleic anhydride-modified polymers and polymers similar thereto. Such polymers are effective adhesives for adhering the polyolefin layer to the EVOH layer and also a viscosity similar to the above-described EVOH and polyolefin layers. The preferred adhesives for use in this invention are maleic anhydride-modified polyolefins. Examples of such polymers are the Admer® QF-500 series manufactured by Mitsui Petrochemical Company, the Modic® P-300 series manufactured by Mitsubishi Petrochemical Company, and Plexar® adhesives manufactured by Chemplex.

The process for the manufacture of a biaxially oriented three or more layer composite barrier sheet consists of four distinct steps which together comprise a relatively simple continuous operation. First, the composite sheet, consisting of polypropylene, for example, an adhesive layer, and an EVOH barrier layer, is formed by co-extrusion of the above components. One way of accomplishing this is to use three extruders and have the materials fed into a combining feed block. Within the feed block, the materials are layered to form the multi-layer melt stream wherein the adhesive is interposed between the polypropylene and the EVOH. The melt stream is fed into a slot cast sheet die or other type of die to form the multi-layer sheet. As the sheet exits the die, it is immediately cooled by use of a cooling drum or a water bath to a temperature satisfactory to maintain a 25 percent crystallinity rate in the EVOH material.

The 25 percent crystallinity rate can be obtained by maintaining the temperature of the cooling medium at 30° to 40° C. If the crystallinity of the EVOH is higher than 25 percent at this point in the process, the EVOH becomes too stiff to stretch properly in the orientation process and it will merely break apart. It is preferable that the crystallinity of the EVOH should be at least about 20 percent in order to obtain sufficient crystallinity in the final product.

Immediately after cooling, the composite sheet is fed into an apparatus adapted for biaxial orientation of plastic material. Any such apparatus can be used in the present invention. One example would be to feed the composite sheet into a set of differential speed heated rollers to stretch the sheet in the longitudinal direction to a degree of about 2:1 to about 4:1. Next, the sheet can be fed to a tenter frame where it is stretched in the transverse direction to a degree of about 3:1 to about 7:1.

If the degree of longitudinal orientation is less than about 2:1, then uneven orientation occurs, and if it is more than about 4:1, then fracture of the sheet occurs. If the degree of orientation in the transverse direction is less than about 3:1, then uneven orientation occurs, and more than about 7:1, then fracture of the sheet occurs. If polypropylene is used as the polyolefin layer, then it is preferred that the machine direction orientation rollers be at a temperature of from about 130° to about 140° C. and that the tenter frame for transverse orientation be at about 150° to about 160° C. If propylene ethylene copolymers are used in the polyolefin layer, then the machine direction roller temperature should be about 125° to about 130° C. and the tenter frame temperature should be about 130° to about 135° C.

After the sheet has been biaxially oriented, it is subjected to a heat setting treatment which allows the EVOH to crystallize. The crystallizing of the EVOH

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imparts high barrier properties to the EVOH layer and thus to the composite film. Any known heat setting method can be used, but one example of such a method is to pass the biaxially stretched sheet over a series of heated rolls.

It is highly preferred that the ratio of the thickness of the adhesive to the thickness of the polyolefin layer be about 1:8 to about 1:15. If the ratio is less than about 1:8, then poor adhesion between the EVOH and adhesive occurs, preventing satisfactory orientation. If the ratio is more than about 1:15, then uneven flow distribution of the adhesive occurs and the adhesion is poor.

EXAMPLES

The materials used in all of the following examples are:

Polypropylene:

Homopolymer - Solvay Eltex HP405, 3.8 melt flow rate

Copolymer - Solvay KS400, 5.7 melt flow rate (4% ethylene, 96% propylene)

Ethylene Vinyl Alcohol Copolymer:

Eval® "F" Grade resin made by Kuraray Co., Ltd. - 1.5 melt index

EVAL® "E" Grade resin made by Kuraray Co., Ltd. - 5.6 melt index

EVAL® "G" Grade resin made by Kuraray Co., Ltd. - 15.1 melt index

Adhesive:

Admer® QF500B - 4.2 melt flow rate (a maleic anhydride-modified polypropylene)

All of the following examples attempted to produce a biaxially oriented five layer composite barrier sheet of ABCBA construction according to the same general process consisting of the following four distinct steps:

1. A five layer composite sheet was co-extruded by the use of three extruders. The sheet consisted of a polyolefin (A layer), an adhesive layer (B layer), an EVOH layer (C layer), another adhesive layer (B layer), and another polyolefin layer (A layer). The materials were fed into a combining feed block where they were layered to form the five layer melt stream of ABCBA construction. This melt stream was then fed into a slot cast sheet die to form the five layer sheet. As the sheet exited the die, it was immediately cooled by the use of a cooling drum, or in some cases a water bath, to a temperature which maintained a 25 percent crystallinity rate in the EVOH material.

2. Immediately after cooling, the composite sheet was fed into a set of differential speed heated rolls (MDO) which stretched the sheet in the longitudinal direction.

3. After exiting the differential speed heated rollers (MDO), the sheet was fed to a tenter frame. In the tenter frame, the sheet was stretched in the transverse direction.

4. After the sheet was biaxially stretched, it was passed over a series of heated rolls which imparted a heat setting to the composite sheet and allowed the EVOH layer to crystallize. The crystallizing of the EVOH imparted high barrier properties to the composite sheet.

The following examples specify which materials were used. The orientation of the extruders was as follows in all cases:

Extruder #1: Always polypropylene

Extruder #2: Always EVOH

Extruder #3: Always Adhesive

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EXAMPLES

In all cases in the following examples, the crystallinity of the EVOH material as it exited the die was maintained below 25%. The crystallinity ranged from 18 to 22% in the examples. The method of determination of the percent crystallinity is based upon the linear relationship between the percent crystallinity and the density of the film. The percent crystallinity is empirically determined by measuring the density of the total amorphous portion and the total crystalline portion of a particular grade of EVOH film and using this information in the formula set out below.

The density is first measured by any acceptable method such as ASTM D1505-68. Next, the total amorphous and total crystalline portions of the EVOH are separated and their densities measured according to the same procedure. For the three grades of EVOH used in the following examples, the densities of the amorphous and crystalline portions are as follows:

TABLE

Grade	Density of Amorphous Portion	Density of Crystalline Portion
E Grade	1.110	1.148
F Grade	1.163	1.200
G Grade	1.094	1.130

The above densities are considered constants because they do not change. The film density will change depending upon the degree of the quenching treatment. In the following formula FD is the film density, AD is the amorphous density constant, and CD is the crystalline density constant. The percent crystallinity of a film is determined by:

$$\% \text{ Crystallinity} = \frac{FD - AD}{CD - AD} \times 100$$

Thus, it is clear that the percent crystalline increases linearly as the density of the film increases. The crystallinity of the film can be controlled by controlling the density of the film. This is what takes place in the quenching step.

EXAMPLE I

Materials:	Homopolypropylene EVOH "E" Grade Adhesive
Extruder #1:	Melt Temp. 260° C., RPM (revolutions per minute) 117.5
Extruder #2:	Melt Temp. 190° C., RPM 25
Extruder #3:	Melt Temp. 185° C., RPM 29.5
Feedblock Temperature:	200° C.
MDO Rolls Temperature:	120° C.
Tenter Temperature:	165° C.
MDO Orientation:	2.0:1
Transverse Orientation:	3.0:1

The stretched film exhibited a fishnet effect due to the fibrillation of the EVOH layer.

EXAMPLE II

Using the same conditions and materials as in Example I, except that the RPM of Extruder #2 (EVOH) was reduced to 15 and the machine direction (MD) orientation was increased to 3.0:1, the same fishnet appearance was evident.

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EXAMPLE III

Starting with the conditions and materials in Example II, the degree of MD orientation was varied while the transverse direction (TD) orientation was held constant. As the MD orientation was decreased from 3.0:1 to 2.0:1, the fishnet appearance decreased. At a 1.0:1, MD orientation and a 3.0:1 TD orientation, the fishnet appearance disappeared. This, however, only resulted in a uniaxially (transverse direction) oriented sheet which exhibit non-uniform thickness and poor optical properties.

EXAMPLE IV

In observing the samples from Example I through III, it was noted that the reason for the fibrillation of the EVOH layer might have been due to the lack of adhesion between the PP and EVOH layers. To investigate this, the conditions and materials used in Example I were selected as a base point. The melt temperature of the adhesive layer was increased in increments of 5° C. until the melt temperature was the same as that of the polypropylene. It was noted that the adhesion became better as the temperature was increased. However, fibrillation of the EVOH layer was still present.

EXAMPLE V

Materials:	Copolymer Polypropylene EVOH "E" Grade Adhesive
Extruder #1:	Melt Temp. 240° C., RPM 95
Extruder #2:	Melt Temp. 190° C., RPM 15
Extruder #3:	Melt Temp. 260° C., RPM 50
Feedblock Temperature:	180° C.
MDO Rolls Temperature:	120° C.
Tenter Temperature:	165° C.
MDO Orientation:	2.4:1
Transverse Orientation:	4.0:1

The initial trials exhibited minor fibrillation of the EVOH layer and uneven orientation of the polypropylene layer. The RPM of the EVOH layer were increased to 30 to increase the thickness. Fibrillation still resulted. The thicknesses of the various layers were increased in increments of 0.5 times the original up to two times the original. There was no appreciable effect on fibrillation. Orientation temperatures were varied until a limit on the low end was reached where transverse stretching would not occur and on the high end until the polypropylene would stick to the tenter frame clips. Fibrillation still was evident. The conclusion reached from the first five examples was that EVOH "E" grade could not be satisfactorily biaxially oriented.

EXAMPLE VI

Materials:	Copolymer Polypropylene EVOH "G" Grade Adhesive
Extruder #1:	Melt Temp. 240° C., RPM 95
Extruder #2:	Melt Temp. 185° C., RPM 20
Extruder #3:	Melt Temp. 250° C., RPM 75
Feedblock Temperature:	185° C.
MDO Rolls Temperature:	120° C.
Tenter Temperature:	140° C.
MDO Orientation:	2.8:1
Transverse Orientation:	3.0:1

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The above conditions were the starting conditions. The composite sheet exhibited extreme melt fracture upon exit from the die. This melt fracture was occurring in the EVOH layer and was due to the difference in viscosities of the various components. The difference in viscosities in turn affected the flow properties through the feedblock and die. Various combinations of heat and speed were investigated until the following parameters were reached which in turn resulted in a satisfactory biaxially oriented composite sheet.

Extruder #1:	Melt Temp. 240° C., RPM 95
Extruder #2:	Melt Temp. 200° C., RPM 20
Extruder #3:	Melt Temp. 250° C., RPM 50
Feedblock Temperature:	200° C.
MDO Rolls Temperature:	129° C.
Tenter Temperature:	130° C.
MDO Orientation:	2.0:1
Transverse Orientation:	3.0:1

EXAMPLE VII

<u>Materials:</u>	Homopolypropylene EVOH "G" Grade Adhesive
Extruder #1:	Melt Temp. 260° C., RPM 115
Extruder #2:	Melt Temp. 190° C., RPM 20
Extruder #3:	Melt Temp. 250° C., RPM 80
Feedblock Temperature:	200° C.
MDO Rolls Temperature:	140° C.
Tenter Temperature:	150° C.
MDO Orientation:	4.4:1
Transverse Orientation:	3.0:1

Again, the above conditions were the starting conditions. Although the sheet going into the tenter frame looked good, holes were torn in the sheet during transverse orientation. This indicates either the sheet is too cold or the orientation is too high. Various orientation ratios were investigated from MDO 2.0:1 to 4.0:1 and transverse from 3.0:1 to 5.4:1. It was noted that as the MDO ratio was increased from 2.0:1, the EVOH started to fibrillate. At 4.0:1 MDO ratio, the EVOH was totally fibrillated. Increasing the transverse ratio and holding the MDO at 2.0:1 did not have the same effect.

EXAMPLE VIII

In an attempt to match viscosities and flow rates of the various materials, the following changes were made in the conditions used in Example VII.

Extruder #1:	RPM 85
Extruder #2:	RPM 25
Extruder #3:	RPM 25
Tenter Temperature:	160° C.
MDO Orientation:	3.0:1
Transverse Orientation:	4.2:1

Using these conditions, an excellent biaxially oriented sheet was produced. The properties of this sheet are shown in the Table. Orientation ranges from MDO 2.0:1 to MDO 4.0:1 and transverse 3.0:1 to 7.0:1 were studied and satisfactory sheets were produced. The properties of two different films made hereunder are shown in the Table.

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EXAMPLE IX

To further investigate the effects of parameters on the ability to orient the sheet, the following was studied:

To determine the effect of Adhesive thickness: The PP RPM was held constant. The adhesive RPM was decreased in 5 RPM increments to 25 RPM. At 25 RPM, fibrillation occurs.

To determine the effect of PP thickness: The adhesive RPM was held constant. The PP RPM was decreased to 70 RPM. Uneven flow distribution occurred. The adhesive RPM was set at 25 RPM. The PP RPM was 70. Uneven flow distribution occurred.

EXAMPLE X

<u>Materials:</u>	Homopolypropylene EVOH "F" grade Adhesive
Extruder #1:	Melt Temp. 260° C., RPM 85
Extruder #2:	Melt Temp. 210° C., RPM 25
Extruder #3:	Melt Temp. 250° C., RPM 50
Feedblock Temperature:	210° C.
MDO Rolls Temperature:	140° C.
Tenter Temperature:	160° C.

MDO orientation from 2.0:1 to 3.0:1 and transverse orientation at 3.0:1 were attempted and fibrillated film resulted. Changes in Extruder #1 RPM to 80 and Extruder #2 RPM to 40 did not have any effect. Various temperature conditions did not have any effect. The conclusion was the EVOH "F" grade could not be satisfactorily biaxially oriented.

Final Thickness

This is a determination of the thickness of even layer in the five layer composite sheet. The film was characterized by both light microscopy and scanning electron microscopy (SEM) techniques. For the SEM technique, the samples were notched and fracture. Light microscopy samples were imbedded in LDPE and microtomed in thin sections. By using the thickness of the individual layers, comparisons can be made between the properties of oriented and unoriented films of the same thickness.

O₂ Transmission

It is known that the presence of oxygen causes foods to degrade. The O₂ transmission of structure is a measure of its barrier to the penetration of oxygen to the materials packaged with the film structure. This determination was carried out according to ASTM Standard D3985-81.

MVTR

The Moisture Vapor Transmission is an indication of the amount of H₂O that will permeate to the packaged goods or conversely the amount of moisture that can escape from a packaged liquid product. Also the barrier properties of a barrier material are deteriorated by the presence of moisture. Therefore, it is desirable to prevent as much moisture as possible from reaching the barrier layer. This test was carried out according to ASTM Test Methods E398-70.

Ultimate Tensile

The ultimate tensile strength is a measure of the strength of the material. It is the amount of force per square inch of material required to pull it apart. This test was carried out according to ASTM D-882-73, Method A.

Secant Modulus

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The secant modulus is a measure of the stiffness of the material. A stiff material is required to provide good machineability and handling in subsequent packaging operations, and also to provide a crisp feel to packaged products. This method was carried out according to AS, M D-618.

TABLE

Example	Final Thickness	O ₂ Transmission cc/m ² /24 hrs. @ 20° C. 0% RH	MVTR g/m ²	Ultimate Tensile		Secant Modulus	
				MD MPa	TD Mpa	MD Mpa	TD Mpa
Homo-polymer PP	12	12	3.0	80	250	1888	5148
Adhesive EVOH G	1.3 3.5						
Adhesive Homo-polymer PP	1.3 12						
Homo-polymer PP	13	13	3.3	91	238	1575	4089
Adhesive EVOH G	1 2						
Adhesive Homo-polymer PP	1 13						

I claim:

1. A method of producing a biaxially oriented oxygen and moisture barrier film which comprises:

(a) co-extruding

(1) at least one layer of a polyolefin material selected from the group consisting of polyethylene, polypropylene, and copolymers of ethylene with other olefins,

(2) at least one layer of an ethylene vinyl alcohol copolymer with a melt flow rate of at least about 8 grams per 10 minutes, and

(3) at least one adhesive layer

and combining these layers into a composite sheet wherein the adhesive is interposed between the polyolefin layer and the ethylene vinyl alcohol copolymer layers,

(b) immediately cooling the composite sheet so that the crystallinity of the ethylene vinyl alcohol copolymer is no more than about 25 percent, and

(c) biaxially orienting the composite sheet in the longitudinal direction to a degree of about 2:1 to about 4:1 and in the transverse direction to a degree of about 3:1 to about 7:1.

2. The method of claim 1 wherein the ratio of the thickness of the adhesive to the thickness of the polyolefin layer is about 1:8 to about 1:15.

3. The method of claim 1 wherein the composite sheet is cooled in a cooling medium at a temperature of 30° to 40° C. in step (b).

4. The method of claim 1 wherein the longitudinal orientation is carried out at a temperature of from about 130° to about 140° C. and the transverse orientation is carried out at a temperature of from about 150° to 160°

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C. and the polyolefin layer is comprised of polypropylene.

5. The method of claim 1 wherein the longitudinal orientation is carried out at a temperature of from about 125° to about 130° C. and the transverse orientation is carried out at a temperature of from about 130° to 135° C. and the polyolefin layer is comprised of a copolymer of propylene and ethylene.

6. The method of claim 1 wherein the polyolefin layer is selected from the group consisting of polypropylene and copolymers of propylene and ethylene.

7. The method of claim 1 wherein a five layer film is produced comprising two outer polyolefin layers, an inner ethylene vinyl alcohol copolymer layer, and two adhesive layers disposed between the polyolefin layers and the ethylene vinyl alcohol copolymer layer.

8. A biaxially oriented oxygen and moisture barrier film formed by:

(a) co-extruding

(1) at least one layer of a polyolefin material selected from the group consisting of polyethylene, polypropylene, and copolymers of ethylene with other olefins,

(2) at least one layer of an ethylene vinyl alcohol copolymer with a melt flow rate of at least about 8 grams per 10 minutes, and

(3) an adhesive layer

and combining these layers into a composite sheet wherein the adhesive is interposed between the polyolefin layer and the ethylene vinyl alcohol copolymer layers,

(b) immediately cooling the composite sheet so that the crystallinity of the ethylene vinyl alcohol copolymer is no more than about 25 percent, and

(c) biaxially orienting the composite sheet in the longitudinal direction to a degree of about 2:1 to about 4:1 and in the transverse direction to a degree of about 3:1 to about 7:1.

9. The film of claim 8 wherein the ratio of the thickness of the adhesive to the thickness of the polyolefin layer is about 1:8 to about 1:15.

10. The film of claim 8 wherein there are five layers which are comprised of two outer polyolefin layers, an inner ethylene vinyl alcohol copolymer layer, and two adhesive layers disposed between the polyolefin layers and the ethylene vinyl alcohol copolymer layer.

11. The film of claim 8 wherein the polyolefin layer is selected from the group consisting of polypropylene and copolymers of propylene and ethylene.

12. The film of claim 8 wherein the composite sheet is cooled in a cooling medium at a temperature of 30° to 40° C. in step (b).

13. The film of claim 8 wherein the longitudinal orientation is carried out at a temperature of from about 130° to about 14° C. and the transverse orientation is carried out at a temperature of from about 150° to 160° C. when polypropylene is the core layer.

14. The film of claim 8 wherein the longitudinal orientation is carried out at a temperature of from about 125° to about 130° C. and the transverse orientation is carried out at a temperature of from about 130° to about 135° C. when the core layer is a copolymer of propylene and ethylene.

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